

1,1'-Dimethyl-4,4'-bipyridinium-smectites as a novel adsorbent of phenols from water through charge-transfer interactions

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The adsorption of 2,4-dichlorophenol onto the 1,1'-dimethyl-4,4'-bipyridinium-saponite, a smectite group of clay minerals, from dilute aqueous solution occurred effectively through charge-transfer interactions and such interactions resulted in the change in the color of the 1,1'-dimethyl-4,4'-bipyridinium-saponite.

There is a demand for materials with molecular recognition and separation abilities, so that the designing of porous solids from inorganic¹ and organometallic² building units through various synthetic strategies including crystal engineering¹ and molecular imprinting techniques³ has been investigated so far. Organic modification of layered solids is a possible way of producing inorganic-organic hybrid materials with controlled guest binding abilities and nanoporous and hydrophobic nature have been imparted on the surfaces.⁴ In order to meet the requirements to the adsorbents for a wide variety of organic compounds, designing inorganic-organic hybrid materials from the modification of layered solids for variable nanospace geometry and chemistry is worth investigating further.

Here we report the effective adsorption of 2,4-dichlorophenol onto 1,1'-dimethyl-4,4'-bipyridinium(methylviologen; abbreviated as MV²⁺)-saponite, from dilute aqueous solution. The charge-transfer interactions between MV²⁺ and 2,4-dichlorophenol are thought to be a driving force for the adsorption as proposed by the fact that the color of the MV²⁺-saponite changed from colorless to yellow by the adsorption of 2,4-dichlorophenol. Such color-change can be utilized as a measure of the hazardous aromatic compounds in water. The adsorption behavior of phenols (phenol and 2,4-dichlorophenol) onto MV²⁺-smectites (a natural montmorillonite and a synthetic saponite) will be described in the present paper.

MV²⁺-smectites were prepared from sodium-montmorillonite (Kunipia F; obtained from Kunimine Ind. Co., cation exchange capacity (CEC) of 119 meq per 100 g clay⁵) and synthetic sodium-saponite (Sumecton SA; obtained from Kunimine Ind. Co., CEC of 71 meq per 100 g clay⁵) by cation exchange reactions with MV²⁺ dichloride.⁶ The basal spacings of the MV²⁺-smectites were 1.3 nm. The gallery heights of the MV²⁺-smectites were determined to be 0.3 nm by subtracting the thickness of the silicate layer (*ca.* 1.0 nm) from the observed basal spacings. Taking the gallery heights and the size of MV²⁺ (0.63 × 1.34 × 0.3 nm)^{7a} into consideration, the adsorbed MV²⁺ are thought to be arranged as a monomolecular layer with their molecular planes (0.3 nm) parallel to the silicate layers.⁷ The adsorbed amounts of MV²⁺ were determined by the C content (*ca.* 7 and *ca.* 4 mass % for the MV²⁺-montmorillonite and MV²⁺-saponite, respectively) to be 116 meq per 100 g of montmorillonite and 71 meq per 100 g of saponite, showing quantitative ion exchange reaction between sodium ions and MV²⁺.

The adsorption isotherm of 2,4-dichlorophenol on the MV²⁺-saponite from aqueous solution is shown in Fig. 1.⁸ According to the Giles classification,⁹ the isotherm of 2,4-dichlorophenol for the MV²⁺-saponite follows type L, showing strong adsorbate-adsorbent interactions. On the other hand, the adsorption of phenol onto the MV²⁺-saponite yields an S-type

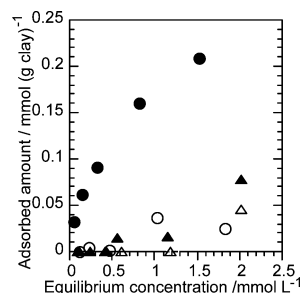


Fig. 1 Adsorption isotherms of phenol (triangle) and 2,4-dichlorophenol (circle) on the MV²⁺-smectites from aqueous solution. Open and filled symbols designate MV²⁺-montmorillonite and MV²⁺-saponite, respectively.

isotherm (Fig. 1), which is represented by initial downward curvature followed by a plateau and then the beginning of a final upswing. S-type isotherms are characteristic of weak adsorbate-adsorbent interactions, causing adsorption at relatively low concentrations to be small.

We expected that the charge-transfer interactions between MV²⁺ and 2,4-dichlorophenol caused the strong adsorbate-adsorbent interactions. Judging from the reduction potential of MV²⁺-smectites¹⁰ and the oxidation potential of 2,4-dichlorophenol,¹¹ the MV²⁺-saponite and 2,4-dichlorophenol act as electron acceptor and donor, respectively, to form a charge-transfer complex. From the Mulliken theory,¹² the energy of the charge-transfer transition in π - π^* complexes corresponds to the energy of the transfer of an electron from the π electronic HOMO of the donor to the π electronic LUMO of the acceptor. It has been known that the donor strongly interacts with the acceptor, if the donor possessed lower ionization potential is used. Considering the position of the absorption bands ascribed to π - π^* electronic transition of an aqueous phenol solution (270 nm) and an aqueous 2,4-dichlorophenol solution (290 nm), the ionization potential of 2,4-dichlorophenol is lower than that of phenol. Therefore, it is thought that the adsorption of phenol was less effective, while the adsorption of 2,4-dichlorophenol onto the MV²⁺-saponite occurred effectively.

The spectroscopic properties of the MV²⁺-saponite-2,4-dichlorophenol supported the above mentioned discussion. Fig. 2

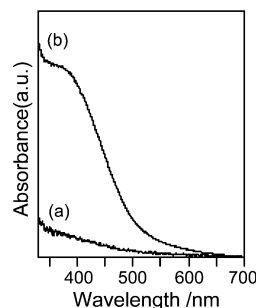


Fig. 2 UV-Vis diffuse reflectance spectra of (a) MV²⁺-saponite and (b) MV²⁺-saponite-2,4-dichlorophenol.

shows the UV-Vis diffuse reflectance spectrum of the MV²⁺-saponite-2,4-dichlorophenol (Fig. 2b), together with that of the MV²⁺-saponite (Fig. 2a). In the spectrum of the MV²⁺-saponite-2,4-dichlorophenol, a new absorption band appeared at around 400 nm. The absorption band was not observed for an aqueous 2,4-dichlorophenol solution (290 nm), the MV²⁺-saponite (at around 280 nm) and an aqueous MV²⁺ dichloride solution (258 nm). It has been known that MV²⁺ dichloride forms charge-transfer complexes with phenols.¹³ The absorption maximum of the MV²⁺ dichloride-2,4-dichlorophenol¹⁴ charge-transfer band in methanol solution appeared at around 370 nm. Thus, the formation of the charge-transfer complex between MV²⁺ and 2,4-dichlorophenol in the interlayer space was shown. The difference in the size and microstructure of the charge-transfer complex in solution and in the interlayer space of clay as well as the interactions with the surface of the silicate layer and the complex was thought to be a possible reason for the slight difference in the absorption maximum. The color-change signature upon the adsorption of 2,4-dichlorophenol on the MV²⁺-saponite can be applied for colorimetric sensing¹⁵ for the purpose of environmental pollutants detector. We recently reported the change in the color of the MV²⁺-smectites by the reactions of neat phenol and 2-naphthol.¹⁶

The organoclay (cetyltrimethylphosphonium-clay) as electrode modifiers of a carbon paste electrode for the electrochemical detection of 2,4-dichlorophenol in water was reported.¹⁷ 2,4-Dichlorophenol can be detected at very low concentrations (20 μM) by using this technique, if compared with the present condition.⁸ It is difficult to recognize 2,4-dichlorophenol from the spectral change in the aqueous suspension of the MV²⁺-saponite at 20 μM of initial concentration because the molar extinction coefficient for the charge-transfer complex of MV²⁺ dichloride-2,4-dichlorophenol is small (ca. 50 L mol⁻¹ cm⁻¹ at 370 nm). A search for the appropriate combination of electron donor and acceptor species is being made.

The adsorption of 3,5-dichlorophenol onto organically modified clays¹⁸ was reported. The adsorption isotherms of 3,5-dichlorophenol from aqueous solution for the trimethylphenylammonium-smectite and the cetyltrimethylammonium-smectite followed type S. The adsorbed amounts of 3,5-dichlorophenol on the trimethylphenylammonium-smectite and the cetyltrimethylammonium-smectite were ca. 0.01 and ca. 0.6 mmol g⁻¹ at the equilibrium concentration of 1 mM, respectively. The adsorbed amount of 3,5-dichlorophenol on the cetyltrimethylammonium-smectite is larger than the maximum adsorption capacity of 2,4-dichlorophenol for the MV²⁺-saponite (0.17 mmol g⁻¹, derived from Langmuir plot of the isotherm (Fig. 1)). The adsorption of chlorinated phenols onto the cetyltrimethylammonium-smectite led to the expansion of the basal spacing. The use of hydrophobic interactions has been effective for the adsorption of chlorinated phenols. The basal spacing of the trimethylphenylammonium-smectite did not change upon the adsorption of chlorinated phenols. The microstructure of the trimethylphenylammonium-smectite (the basal spacing was 1.5 nm) was thought to lead to a size exclusion effect. The charge-transfer interactions are a strong driving force for the adsorption of 2,4-dichlorophenol onto the MV²⁺-saponite, so that L-type isotherm was obtained although the microstructure of the MV²⁺-saponite was analogous to that of the organically pillared smectites reported previously.^{1a,4b,18}

The adsorption isotherms of phenol and 2,4-dichlorophenol for the MV²⁺-montmorillonite from aqueous solution follow type S (Fig. 1). The differences in the adsorption behavior of 2,4-dichlorophenol on the MV²⁺-smectites depending on the clay are thought to be due to the layer charge density of smectites as reported for the adsorption of phenol and 4-chlorophenol on the tetramethylphosphonium-montmorillonites.¹⁹ The adsorption of phenol and 4-chlorophenol on the tetramethylphosphonium-montmorillonite derived from a rela-

tively low-charged clay (CEC = 90 meq per 100 g clay) occurred, while the adsorption of these two phenols on the tetramethylphosphonium-montmorillonite derived from a relatively high-charged clay (CEC = 120 meq per 100 g clay) did not occur. Relatively low layer charge density of the saponite (CEC = 71 meq per 100 g) led the relatively large pore volume in the interlayer space, which correlates with the adsorption capability of 2,4-dichlorophenol.

This work demonstrated that charge-transfer interaction is a possible driving force for the adsorption of 2,4-dichlorophenol on the MV²⁺-saponite from aqueous solution. Such interactions can be precisely controlled by the change in the molecular structures of both adsorbates and adsorbents, so that the effective adsorption exhibited by the MV²⁺-saponite for 2,4-dichlorophenol was achieved. Molecular sieving effects for the adsorption of 2,4-dichlorophenol on the MV²⁺-smectites may arise from the surface layer charge density. Combining these strategies, efforts are being made using clays with different origins and organic groups with different π-conjugated systems to construct hybrid materials with precisely controlled adsorptive properties.

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